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**(54) Method of manufacturing silicon sulfide**

(57) Silicon sulfide is manufactured from the fine powder of silicon covered thoroughly with sulfur at lower temperature less than 800°C in vacuum.

To produce the silicon sulfide, silicon should be ground in the non-oxidizing condition to prevent the formation of silicon oxide layer that should cause to retard the reaction or necessitate higher temperature. The silicon powder is dispersed sufficiently in the molten sulfur. At this time, the quantity of sulfur added needs more than 1.1 times in comparison with the stoichiometric quantity of silicon sulfide.

All surface of silicon powder should be covered with sulfur to avoid sintering between silicon particles in the process of heating.

## Description

This invention relates to a method of manufacturing silicon sulfide.

Some methods for synthesizing silicon sulfide have been known as follows:

- (1) to react silicon oxide with aluminum sulfide in atmosphere of inert gas,
- (2) thermal cracking of organic silicon compounds,
- (3) to react silicon with hydrogen sulfide in hydrogen atmosphere.

But each method includes some problems to be solved. Namely, in case of said prior art (1), aluminum sulfide is expensive and this method needs essentially higher temperature than 1100°C, in case of said prior art (2), organic silicon compounds are expensive and organic sulfur compounds with stinks are released absolutely in this reaction, and in case of said prior art (3), this method needs high temperature such as more than 1200 °C so that the selection of equipment materials have very serious problems.

Therefore, it is the object to present a method for producing silicon sulfide in which the synthesis of highly pure silicon sulfide is possible at lower temperature so as to expand the width extent of choice of processing apparatus and material therefore, make workability preferable and decrease the energy consumption.

Fine powder of silicon is dispersed into melted sulfur by agitation. Then the obtained mixture consisting of the silicon powder and surplus sulfur is feeded into a vacuum vessel, and heated to produce silicon sulfide.

Silicon sulfide can be manufactured from the fine powder of silicon covered thoroughly with sulfur by the reaction at lower temperature less than 800°C in vacuum. To produce silicon sulfide, silicon should be ground in non-oxidizing condition to prevent the formation of a silicon oxide layer that would cause a retardation of the reaction or necessitate a higher temperature like more than 800°C.

The prepared silicon powder is provided gradually into molten sulfur that is intensely agitated by means of a mechanical agitation and then it is dispersed sufficiently. At this time, the quantity of molten sulfur must be more than 1.1 times of the stoichiometric quantity of silicon sulfide.

If the particle size of silicon powder is very small, a large quantity of sulfur must be added, due to the total surface area becoming awfully large in comparison with larger silicon particle. And also it is difficult to produce the homogeneous silicon powder dispersion in sulfur. In the case of silicon powder having a large surface area by reason of its own shape, the addition of sulfur is also needed much as same.

It is undesirable to reduce the quantity of sulfur, because, if the whole surface area of silicon powder is not covered thoroughly with sulfur, a reaction does not start at lower temperature. Furthermore, the considera-

ble amount of silicon powder should remain, just as it is, on account of sintering strongly between silicon particles. The strong sintering has a tendency to prohibit the reaction of the mixture in spite of higher temperature.

It is also undesirable that the quantity of sulfur is increased more than the stipulation, because the labor and energy are required for a separation of surplus sulfur from the reacted mixture.

Therefore it is preferable, when the quantity of sulfur is in the range of 1.1 to 1.8 times for the stoichiometric quantity of silicon sulfide. In addition, it is better to adjust the quantity of sulfur in the range of 1.1 to 1.5 times.

In the smaller particle size of silicon, this reaction occurs more easy on the condition that each silicon particle disperses homogeneously in sulfur. However, the purity of silicon sulfide decreases, because of having oxidized of the surface of the minute silicon powder. Moreover, there are difficulties that the silicon fine powder easily happens to be dust at handling and does not disperse in melted sulfur well by reason of its flocculation characteristic, and there is a dangerous factor that the fine particles react vigorously.

If the particle size of silicon powder is larger than 100 μm, the necessary quantity of sulfur to cover silicon powder decreases. But its reaction needs to heat at high temperature, for example 800 °C and to maintain its temperature for many hours instead of the possibility of the reduction of sulfur quantity.

The heating temperature depends on the particle size of silicon powder, and the dispersing conditions of silicon particles in melted sulfur. If the heating temperature is under 400°C, this reaction does not start even though enough sufficiently dispersing of silicon and sulfur is present. If the heating temperature is above 800°C, the non-reacted silicon powder is easy to remain as silicon powder being easily sintered by this exothermic reaction.

If this reaction is conducted at high temperature, for example 1000°C, the equipment for synthesis of silicon sulfide becomes expensive. Because the internal pressure in the equipment becomes high depending on the reaction temperature, so the selection of equipment materials is restricted widely in order to suppress the corrosion by sulfur or sulfide.

## EXAMPLE

350 g of highly pure sulfur powder, (6N), was weighted in a stainless steel cup and then the sulfur was melted in an oil bath at 125°C. 100 g of highly pure silicon, (6N), having the particle size of 25 μm in average was weighted and feeded into the molten sulfur gradually, which was agitated by a mechanical mixing apparatus. After that, stirring was continued for one hour in order to cover the silicon surface with sulfur entirely.

This mixture was ground after cooling, and then this granule was put into a quartz tube. Air in the quartz tube was evacuated up to  $10 \times 10^{-6}$  Torr and enclosed.

The quartz tube was positioned in an electric furnace. One part of the quartz tube was maintained at 470 °C and the other part was maintained 700°C, respectively, for 150 hours.

The product was porous and its color was bluish white. According to X-ray diffraction, only silicon sulfide was detected.

#### COMPARATIVE EXAMPLE 1

The example was repeated except that the temperatures of both parts of the quartz tube were kept 350°C. The product had silicon dispersed in sulfur uniformly and seldom reacted.

#### COMPARATIVE EXAMPLE 2

The example was repeated except that one part of the container was maintained at 470°C, the other part was maintained 950 °C. The product was not porous and its color was light bluish white. There were some aggregates, which were probably sintered silicon particles, in the quartz tube.

#### COMPARATIVE EXAMPLE 3

The example was repeated except that the average particle size was 150 µm. The product was porous and its color was light bluish white, though it had some blackish spots. According to X-ray diffraction, silicon sulfide, silicon and sulfur were detected.

#### COMPARATIVE EXAMPLE 4

The example was repeated except that the quantity of sulfur was 230g. The product was porous and had blackish aggregates everywhere.

As described above, silicon powder is dispersed into molten sulfur and covered thoroughly with the sulfur, so silicon sulfide is easily manufactured by heating the mixture consisting of the silicon powder and the sulfur, the method therefore allows a wide range of selection of equipment materials and decreased energy consumption.

If the sulfur surplus is in the range of 1.1 to 1.8 times of the stoichiometric sulfur quantity of silicon sulfide when silicon powder is dispersed into melted sulfur, the silicon powder can be thoroughly covered with melted sulfur, and separation of surplus sulfur from the reacted mixture can easily be done.

If the mixture fed into the vacuum vessel is heated in the range of 400 to 800°C, pure silicon sulfide is manufactured without problems such as high pressure reaction in the vessel, sintering silicon particles and remaining non-reacted silicon powder.

ing:

dispersing silicon powder into molten sulfur by agitation,  
feeding the mixture consisting of the silicon powder and surplus sulfur into a vacuum vessel, and  
heating the mixture to react.

2. The method according to claim 1, wherein said silicon powder has a size of not larger than 100 µm.
3. The method according to claim 1 or 2, wherein said surplus sulfur is in the range of 1.1 to 1.8 times of the stoichiometric sulfur quantity of silicon sulfide.
4. The method according to anyone of the claims 1 to 3, wherein said heating is in the range of from 400 to 800°C.

#### Claims

1. A method of manufacturing silicon sulfide compris-



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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 10 5989

| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |  |   |
|--|--|--|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim  | CLASSIFICATION OF THE APPLICATION (Int.Cl.6)    |
| A  | CHEMIKER ZEITUNG,<br>vol. 107, no. 10, 1983, HEIDELBERG DE,<br>pages 289-290, XP002033551<br>R. G. SOBOTT ET AL.: "Darstellung und<br>Stabilität der Sulfide des Siliciums und<br>ein Vergleich mit den Germaniumsulfiden"<br>* page 290, left-hand column, paragraph 2<br>- paragraph 3; figure 1 * | 1  | C01B33/00                                       |
| A  | DATABASE WPI<br>Week 8246<br>Derwent Publications Ltd., London, GB;<br>AN 82-99476E<br>XP002033553<br>& SU 899 464 B (AS SIBE INORG CHEM) , 23<br>January 1982<br>* abstract *   | 1,3  |   |
| A  | "GMELINS HANDBUCH DER ANORGANISCHEN<br>CHEMIE 8th completely reworked edition<br>SILICIUM Part B System-number 15"<br>1959 , VERLAG CHEMIE, GMBH.<br>WEINHEIM/BERGSTRASSE XP002033552<br>* page 747, line 5 - line 8 *   |  | TECHNICAL FIELDS<br>SEARCHED (Int.Cl.6)<br>C01B |
| The present search report has been drawn up for all claims   |  |  |   |
| Place of search<br>THE HAGUE   |  | Date of completion of the search<br>23 June 1997   | Examiner<br>Brebion, J                          |
| CATEGORY OF CITED DOCUMENTS  |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or<br>after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding<br>document |   |
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